

In Situ Ester–Amide Exchange Reaction Between Polyamide 6 and Ethylene-Vinyl Acetate Rubber During Melt Blending

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ABSTRACT: The ester–amide exchange reaction between polyamide 6 (PA6) and ethylene-vinyl acetate rubber (EVM) with dibutyltin oxide (DBTO) as a catalyst took place during melt blending, leading to the formation of PA6-grafted EVM copolymer (EVM-*g*-PA6) and acetamide-terminated PA6. The exchange reaction extent, expressed by the percentage content of the acetate groups taking part in the exchange reaction, was 5.9 mol %, and the yield of EVM-*g*-PA6 copolymer was 6.8 wt % for PA6/EVM/DBTO (60/40/1) blend at 230°C for 60 min. The number-average molecular weight of PA6 branches in EVM-*g*-PA6 was ~278 g/mol as evaluated from nuclear magnetic resonance spectra. The reaction kinetic parameters were calculated according to a second-order reversible reaction mechanism. The rate constant was dependent on the catalyst concentration, PA6/EVM ratio, and shearing conditions. In this article, the characterized ester–amide exchange reaction between PA6 and EVM will guide the fabrication of novel EVM-based graft copolymers and high-performance PA6/EVM thermoplastic elastomers for engineering applications. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40272.

KEYWORDS: polyamides; blends; copolymers; kinetics

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INTRODUCTION

Reactive compatibilization via exchange reactions of polymers is an effective approach to improve interfacial adhesion and mechanical properties of polymer blends. Some exchange reactions, such as ester–ester, ester–amide and amide–amide reactions, lead to *in situ* formation of copolymers.^{1–4} In a few cases, the exchange reactions may diversely affect the mechanical properties of polymer blends, and should be suppressed.^{5,6} Therefore, the exchange reactions need to be elucidated and well controlled to produce high-performance blends.

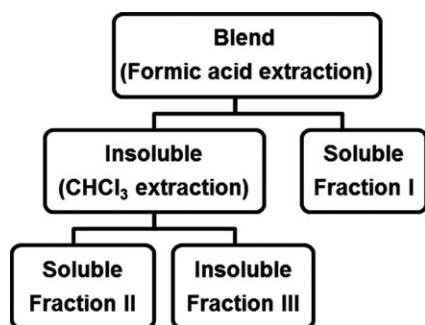
Exchange reactions include the exchange reactions between the main chains of polymers^{1,7,8} such as polyamide (PA)/poly(ethylene terephthalate) (PET),^{1,8} as well as those between the main chains of a polymer and the side groups of another polymer, such as the reaction between the main chains of polycarbonate (PC) and the pendant acetate groups of ethylene-vinyl acetate (EVA) copolymer.⁹ For the main-chain exchange reaction between the amide groups and carbonate groups of PA6 and PC, it only occurs at above 300°C, whereas the reaction between amino end groups of PA6 and carbonate groups of PC actually

occurs at 240°C.^{10,11} A block copolymer was formed during the exchange reaction between PC and amino-terminated PA6, and only 2% of the block copolymer greatly improved the compatibility of PA6 and PC. *p*-Toluenesulfonic acid (TsOH) could accelerate the exchange reaction between PET and PA66, and increased the exchange reaction extent up to 23.3%.^{12,13} TsOH reacted with PET to form PET oligomers with carboxyl end groups and further reacted with PA6 to produce PA6/PET copolymer.⁸ TsOH also accelerated the ester–amide exchange reaction between poly(butylene succinate) and poly(hexamethylene isophthalamide-*co*-terephthalamide),⁷ and improved their compatibility. Terephthalic acid could catalyze the exchange reaction between PET and poly(*m*-xylene adipamide),¹ obtaining semicrystalline block copolymers in 45 min and random copolymers in 75 min. Catalysts are usually needed for exchange reactions of polymers.

Ester–ester exchange reactions between side groups of EVA^{9,14–18} or poly(methyl methacrylate)^{19,20} and the main chains of other polymers, such as PC⁹ and polyesters,^{17,18} were reported. To our knowledge, few publications concerned the ester–amide

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Scheme 1. Extraction and separation procedure of the PA6/EVM/DBTO (60/40/1) blend.

exchange reactions between the main chains of polyamides and the side groups of vinyl polymers prepared by free radical polymerization. The reactions should be important for preparations of novel graft copolymers based on polyamides and vinyl polymers. The study on the mechanism of the reactions is of important theoretical meaning.

PA6 and ethylene-vinyl acetate rubber (EVM) with high vinyl acetate content (over 40%) are widely used important plastic and elastomer, respectively. EVM was usually blended with other rubbers to prepare high-performance elastomer blends.^{21–23} In our group, we used EVM as impact modifier of PA1010^{24–27} to improve the toughness of PA1010. With the EVM content of over 60 wt %, we also prepared PA/EVM thermoplastic elastomers through reactive processing^{28,29} and the thermoplastic elastomers behaved excellent comprehensive properties. However, there are limited studies on PA6/EVM blends in terms of the reactive compatibilization and physical properties. Generally, additional compatibilizers such as ethylene-vinyl acrylic copolymer and maleated EVA are needed for PA6/EVA blends to improve their compatibility and mechanical properties.^{30–37} In our previous study, we found that the ester–amide exchange reaction between PA6 and EVM can be a new method for *in situ* compatibilization of PA6/EVM blends or preparation of EVM-based graft copolymers. In this article, the exchange reaction between PA6 and EVM at elevated temperatures was investigated in detail. Dibutyltin oxide (DBTO) is used as the catalyst as it is more effective and mild in facilitating ester–amide exchange reactions^{38,39} when compared with TsOH,^{7,8,12,13} terephthalic acid,¹ and sodium *p*-toluenesulfonate.⁴⁰ The effects of DBTO content, PA6/EVM ratio, and rotor rotation rate on the exchange reaction were studied. The reaction products were quantitatively characterized for the analysis of exchange reaction mechanism.

EXPERIMENTAL

Materials

PA6 (1013B, number-average molecular weight of 25,000) was produced by UBE Chemical, Japan. EVM (Levapren 400), with $ML_{1+4}^{100^\circ\text{C}}$ of 20 and a vinyl acetate content of 40 wt %, was kindly supplied by Lanxess Deutschland GmbH, Germany. DBTO with a purity of 98%, and deuterated solvents (CDCl_3 and CF_3COOD) were purchased from Adamas-Beta Reagent, Switzerland. Chloroform, formic acid, ethanol, NaOH, xylene,

m-cresol, methanol, and *N*-methyl acetamide (NMA) were purchased from Sinopharm Group Chemical Reagent, China. *cis*-Polybutadiene (PB, BR9000) with $ML_{1+4}^{100^\circ\text{C}}$ of 45 was produced by China Petroleum & Chemical.

Preparation of PA6/EVM Blends via Melt Blending

PA6 and EVM were first vacuum-dried for 12 h at 100 and 60°C, respectively. PA6/EVM/(DBTO) mixtures were compounded using a Haake rheometer at a rotor speed of 60 rpm. For the study on exchange reaction kinetics, the compounding time and temperature varied from 10 to 80 min and 230 to 250°C, respectively. PA6/EVM ratio varied as 60/40, 50/50, and 40/60. For PA6/EVM (60/40) blend, DBTO content varied from 0 to 1 wt % of the blend.

For comparison, PA6/EVM (60/40) blend was also prepared by solution blending. Two grams of PA6/EVM/DBTO (60/40/variable) was dissolved in 100 mL *m*-cresol/xylene (1/1 v/v) mixed solvent. The resultant solution was poured into 500 mL isopropanol under stirring for 20 min and then filtrated. The precipitate was washed with isopropanol for several times and vacuum-dried at 80°C for 72 h. The resultant PA6/EVM blend was heat-treated by using a differential scanning calorimeter (DSC; Q2000, TA Instruments, USA). It was heated from 40 to 250°C at 200°C/min in nitrogen and hold isothermally at 250°C for different time, and was characterized by ¹H NMR.

Hydrolysis of EVM

A total of 0.5 g EVM was dissolved in 20 mL xylene at 80°C in a 50-mL three-necked flask equipped with a magnetic stirrer and a reflux condenser, and then 2.0 mL NaOH–ethanol solution (2.0 mol/L) was added and reacted for 1 h; 100 mL ethanol was poured into the three-necked flask under stirring at room temperature. The resultant precipitate was filtrated and washed with ethanol for several times and finally vacuum-dried.

Extraction of the Copolymer

A total of 2.0 g PA6/EVM (60/40) blend was dissolved in 60 mL formic acid to form a suspension at room temperature under stirring for 24 h. Formic acid is a good solvent for PA6. After filtration, the suspension was divided into a clear solution and

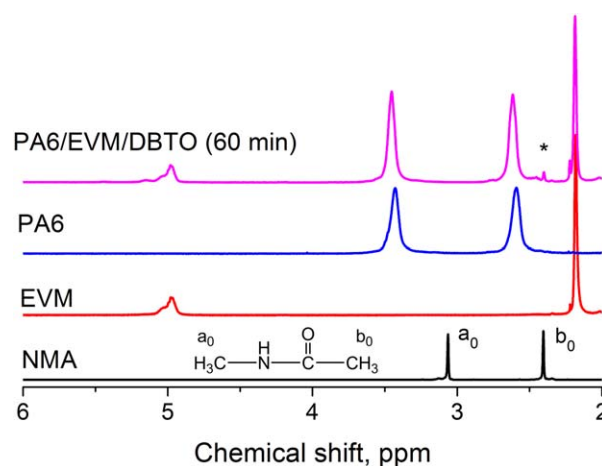
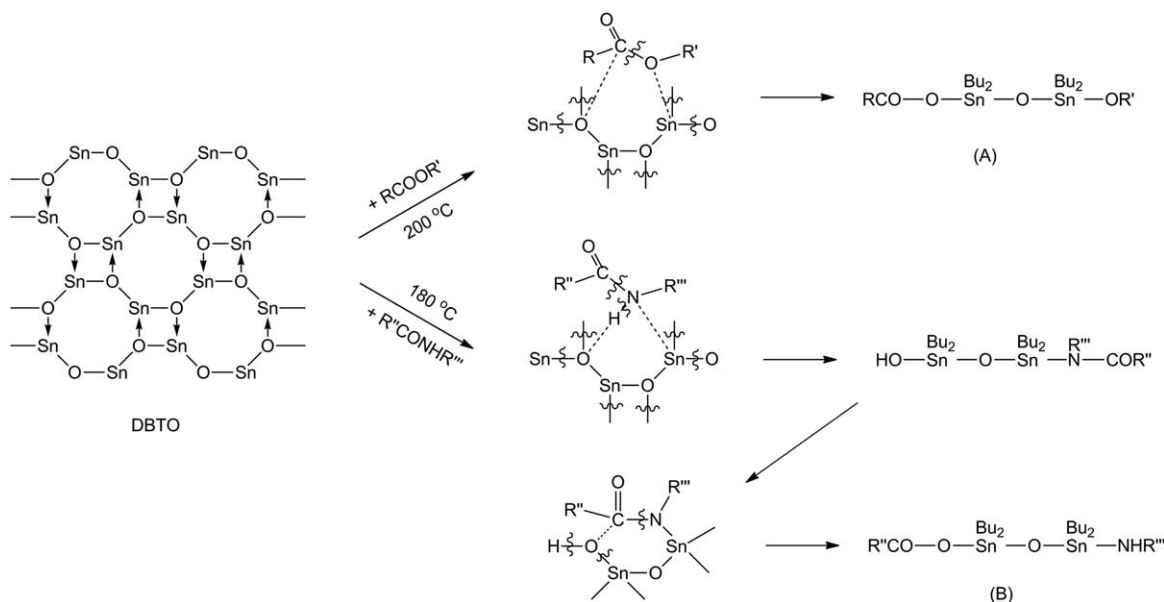


Figure 1. Sections of the ¹H NMR spectra of NMA, EVM, PA6, and PA6/EVM/DBTO (60/40/1, 60 min) blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. Schematic diagram of catalyzing exchange reaction mechanism in the presence of DBTO.

an insoluble part. The clear solution was poured into 300 mL methanol to get a precipitate, which was washed with methanol for several times and vacuum-dried at 100°C for 12 h, noted as Fraction I. The insoluble part was vacuum-dried at 60°C for 24 h and then extracted with CHCl_3 in a Soxhlet apparatus for 72 h to get a solution and a residue. CHCl_3 is a good solvent for EVM. The solution was dried to obtain Fraction II, which should be the unreacted EVM because it is soluble in CHCl_3 and insoluble in formic acid. The residue was vacuum-dried at 60°C for 6 h and named as Fraction III. The extraction procedure is summarized in Scheme 1.

Characterization

Liquid ^1H NMR spectra were recorded by using a MERCURY plus 400 (Varian, USA) with $\text{CDCl}_3/\text{CF}_3\text{COOD}$ (1/1 v/v) as a solvent. Chemical shifts were given in ppm in reference to internal tetramethylsilane (TMS).

Infrared spectra were obtained by using a Spectrum 100 Fourier transform infrared spectra (FTIR) Spectrometer (Perkin Elmer, USA).

Glass transition temperature and melting behavior were characterized by using a DSC (Q2000, TA Instruments) at 20°C/min in nitrogen. A sample was heated from 40 to 260°C to eliminate previous thermal history, then cooled down to -70°C, and finally heated to 260°C.

Thermal stability was characterized by using a thermogravimetric analyzer (Q5000, TA Instruments). A sample was heated to 120°C under nitrogen atmosphere and hold isothermally for 10 min, and then were heated to 240, 260, 280, or 300°C at 20°C/min and hold isothermally for 60 min.

The grafting degree was determined by elemental analysis of the EVM-g-PA6 copolymer in an Elemental Analysis—Stable Isotope Ratio Mass Spectrometer (Vario EL III/Isoprime, Elementar, Germany). The nitrogen content (x) in the copolymer was

measured and then the PA6 content in the EVM-g-PA6 copolymer can be estimated from the equation that PA6 content = $113x/14$.

Blend samples were cryogenically fractured in liquid nitrogen, and their fracture surfaces were observed using scanning electron microscopy (SEM, HITACHI-S-2150, Japan). The fracture surfaces were etched with acetone or formic acid for 12 h to remove the EVM or PA6 phase before observation.

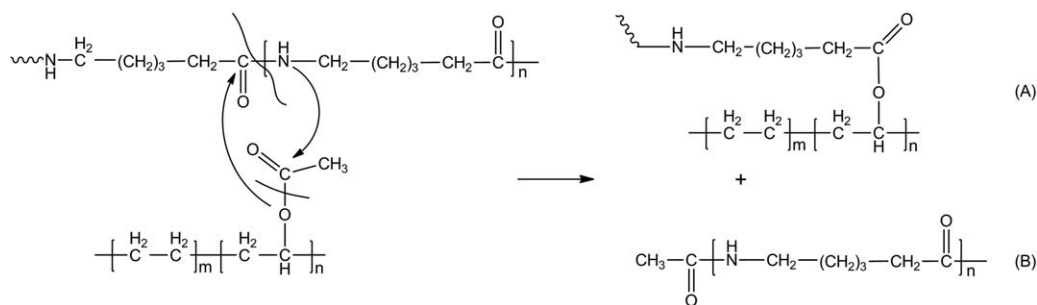
Tensile properties were measured using a universal test machine (Instron 4465, USA) at a crosshead speed of 20 mm/min for the PA6/EVM (60/40) blends. The dumbbell specimens were 75 mm in length, 4 mm in width, and 1 mm in thickness according to ASTM D 638.

RESULTS AND DISCUSSION

Ester–Amide Exchange Reaction

Exchange Reaction Mechanism. PA6/EVM/DBTO (60/40/1, 60 min) blend was prepared by melt compounding at 230°C for 60 min and characterized by ^1H NMR as shown in Figure 1, and the assignments of the chemical shifts of protons are listed in Supporting Information Table S1. Compared with PA6 and EVM, the blend has a new peak at 2.40 ppm in its NMR spectrum. NMA is used as a reference compound to allocate the assignment of the peak. The two strong peaks at 2.40 and 3.06 ppm in the ^1H NMR spectrum of NMA correspond to the chemical shifts of methyl protons adjacent to carbonyl group and amino group, respectively. So, the new peak at 2.40 ppm for the blend should correspond to the methyl protons adjacent to amide carbonyl group by considering the same chemical environment of protons in the two molecular structures of NMA and the blend. Only the exchange reaction can lead to the formation of acetamide groups for the PA6/EVM blend.

In the presence of ester and amide groups, DBTO reacts with ester and amide groups through insertion of [Sn–O] link at



Scheme 3. Schematic diagram of ester–amide exchange reaction between PA6 and EVM.

elevated temperatures as shown in Scheme 2, generating the disannoxane intermediate species, 1-alkoxy-3-acyloxytetrabutyl disannoxane (A, B), which acts as the catalytic species for the exchange reaction between free ester or amide groups and disannoxane,^{38,41,42} and finally leads to the exchange reaction of ester and amide groups. The reaction mechanism for the ester–amide exchange reaction between PA6 and EVM is proposed in Scheme 3. The reaction between the amide groups in PA6 and the ester groups in EVM during compounding at 230°C for 60 min led to the formation of two polymers: EVM-g-PA6 copolymer (A) and acetamide-terminated PA6 (B). To verify the mechanism for PA6/EVM blend, a selective extraction method (Scheme 1) was used to separate EVM-g-PA6 copolymer from PA6 and EVM, and their structure was characterized by ¹H NMR (Figure 2). Because Fraction I is a soluble component in formic acid (Scheme 1), it should be PA6 including the acetamide-terminated PA6 (B in Scheme 3). Fraction I exhibits three signals (*a*, *b*, *c'*) at 3.45, 2.65, and 2.40 ppm, in which the peak at 2.40 ppm indicates the existence of acetamide-terminated PA6. Because Fraction III is not soluble in either formic acid or chloroform, it should be the EVM-g-PA6 copolymer formed during melt compounding.

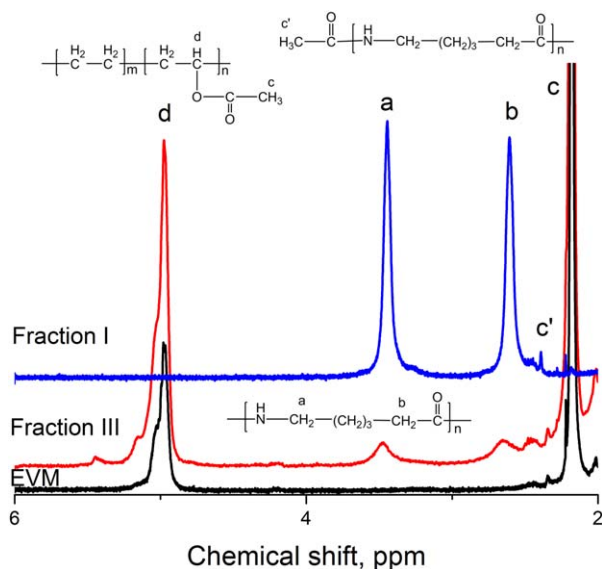


Figure 2. Sections of the ¹H NMR spectra of extracted fraction from PA6/EVM/DBTO (60/40/1, 60 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fraction III shows four signals (*a*, *b*) at 3.45 and 2.65 ppm and (*c*, *d*) at 2.18 and 4.98 ppm, which are assigned to PA6 and EVM, respectively. The extraction experiment and ¹H NMR spectrum support the formation of EVM-g-PA6 copolymer. As further characterized by FTIR (Figure 3), Fraction III exhibits characteristic absorption peaks at 1739 cm⁻¹ (assigned to C=O), 1638 cm⁻¹ (NHC=O), 1545 and 3300 cm⁻¹ (N–H), and 1260–1280 cm⁻¹ (C–N), indicating the coexistence of EVM and PA6 structure in Fraction III. The results in Figures 1–3 confirm the ester–amide exchange reaction mechanism proposed in Scheme 3.

Side Reactions of EVM at Elevated Temperatures. Hydrolysis or elimination of acetate groups of EVM may occur during melt compounding of PA6/EVM blends as side reactions. To qualitatively analyze the reactions, EVM was totally hydrolyzed into ethylene-vinyl alcohol copolymer (EVOH) with NaOH as a catalyst. The FTIR and ¹H NMR spectra of the resultant EVOH are shown in Figure 4. By comparing the FTIR spectrum of EVM and EVOH in Figure 4(a), the characteristic absorption peaks at 1739 cm⁻¹ (assigned to C=O) and 1242 cm⁻¹ (assigned to OC–O) disappear after hydrolysis of EVM, and a broad absorption peak at 3350 cm⁻¹ assigned to hydroxy group emerges. In Figure 4(b), the signal peaks (*α'*) at 5.16, 5.31, and 5.37 ppm in the EVOH spectrum correspond to the protons of methine adjacent to hydroxyl groups. The signal peaks (*β*) at

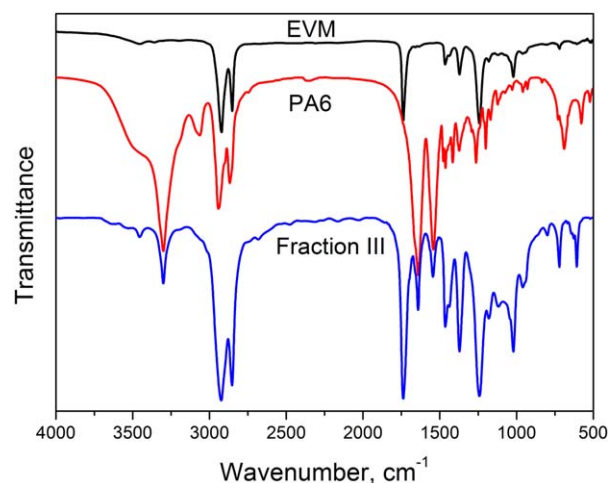


Figure 3. FTIR spectra of extracted Fraction III from PA6/EVM/DBTO (60/40/1, 60 min) blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

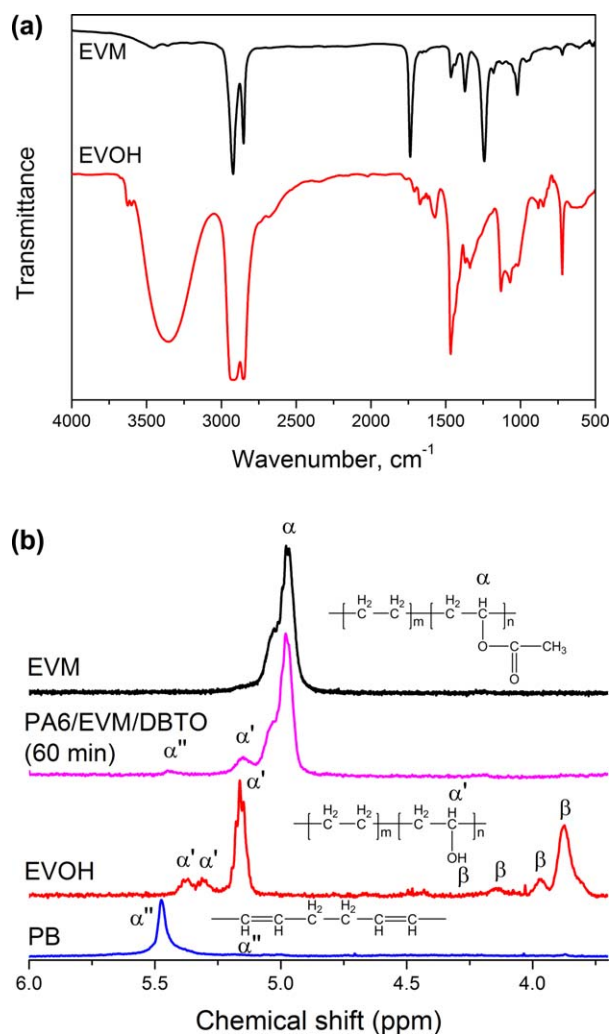


Figure 4. Characterization results of the hydrolyzed EVM (EVOH): (a) FTIR spectra and (b) ^1H NMR spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3.87, 3.97, and 4.14 ppm correspond to the protons of hydroxyl groups. The small peaks should be resulted from heterogeneous structural sequences and configurations of EVOH macromolecules.^{43,44}

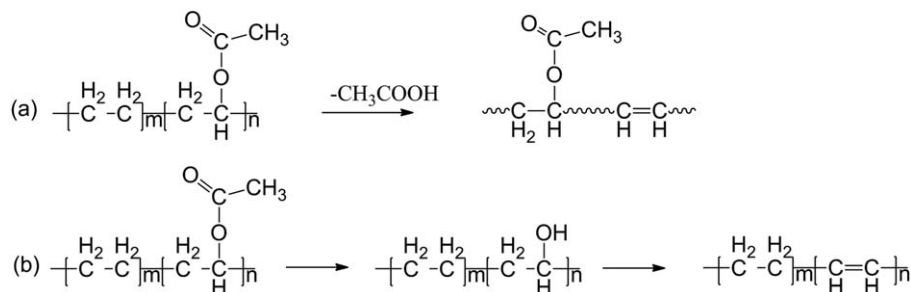
In Figure 4(b), PA6/EVM/DBTO (60/40/1, 60 min) blend has two small signal peaks at 5.16 and 5.45 ppm. The peak at 5.16 ppm corresponds to the protons of methine adjacent to hydroxyl groups, suggesting the existence of hydroxyl groups in

EVM. The peak at 5.45 ppm indicates the existence of carbon-carbon double bonds in EVM, in comparison to the spectrum of PB. Therefore, there should be three reactions during melt compounding of PA6/EVM blends: (i) hydrolysis of acetate groups of EVM at elevated temperatures; (ii) elimination of hydroxyl groups (Scheme 4); and (iii) exchange reaction between PA6 and EVM (Scheme 3). The first two reactions are side reactions, and will be considered for calculation of kinetic parameters and grafting ratio of PA6 in EVM-g-PA6 copolymer.

Effects of Reaction Condition on the Exchange Reaction. The extent of exchange reaction is assessed by the proton signal intensity ratio between the peaks at 2.40 and 3.45 ppm ($2I_{2.40}/3I_{3.45}$), corresponding to the chemical shifts of methyl protons of terminal acetamide groups and methylene protons adjacent to amide amino groups in the PA6, respectively, in the ^1H NMR spectra of the blends [Figure 5(a)]. By using this ratio, the effects of side reactions of acetate groups in EVM at elevated temperatures could be avoided.

For ester–amide reactions, such as those between PET/PA^{1,40} or PBS/PA,⁷ the copolymer formed at interfaces was commonly hard to be isolated owing to their low quantity. Here, the exchange reaction extent increased (Table I) with the addition of DBTO and increasing reaction time; therefore, the formed graft copolymer was extracted successfully, and the content of EVM-g-PA6 (Fraction III) was increased from 2.0 to 6.8% with increasing reaction time from 10 to 60 min for PA6/EVM/DBTO (60/40/1) blend (Supporting Information Table S2). Compared with the yield of graft copolymer (about 25 wt %) formed through transesterification between EVA copolymer and polylactide,¹⁶ the yield of EVM-g-PA6 copolymer through ester–amide reaction is relatively low. The extracted copolymer is further characterized by DSC [Figure 5(b)], and its glass transition temperature is -29°C , nearly the same as that of EVM. The enthalpy at melting temperature of 220°C becomes higher when the reaction time is 40 min or longer, which means the reaction extent increases. This phenomenon is consistent with the results in Figure 5(a).

The effects of reaction temperature and time on the exchange reaction of PA6/EVM/DBTO blends are investigated by ^1H NMR [Figure 5(c)]. When the blends were heated at temperatures over 280°C for 100 min, the EVM fraction could not be dissolved in $\text{CDCl}_3/\text{CF}_3\text{COOD}$ mixed solvent owing to the insoluble product of EVM from the side reactions. From thermogravimetric analysis, EVM underwent obvious elimination of acetate groups at temperatures over 260°C (Supporting Information Figure S1).



Scheme 4. Schematic diagram of side reactions for EVM in PA6/EVM blends at elevated temperatures.

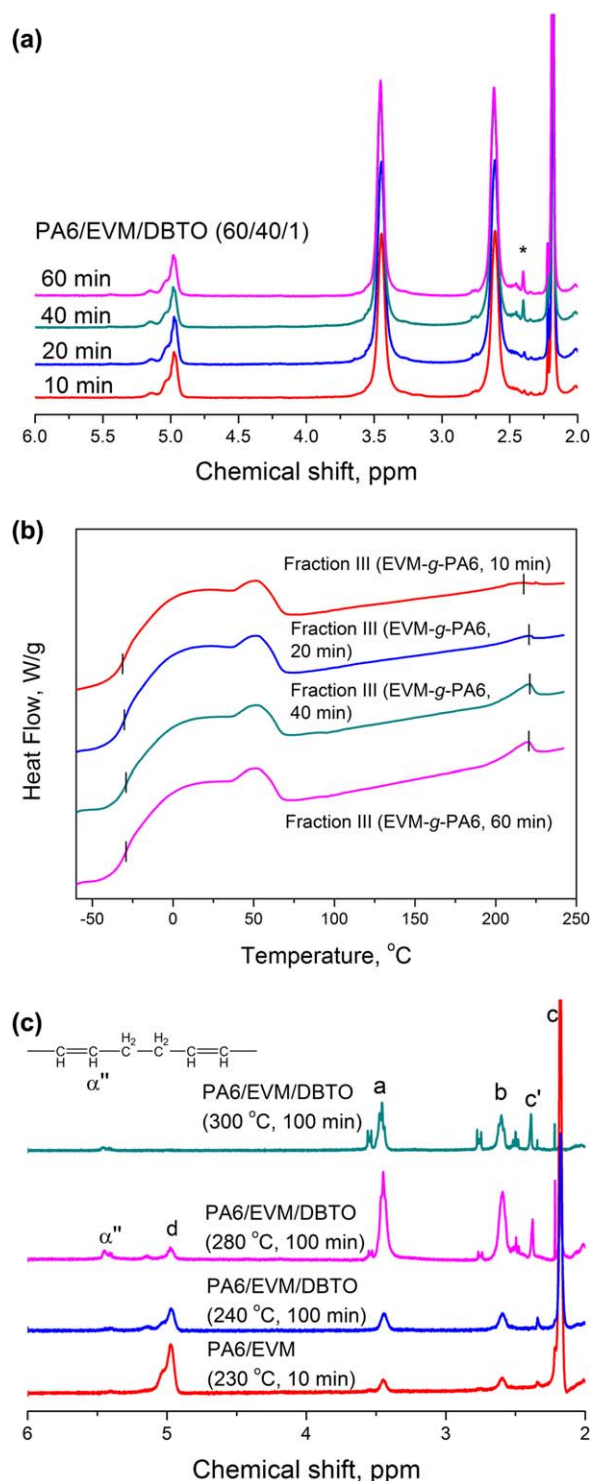


Figure 5. Effects of reaction temperature and time on the exchange reaction extent of PA6/EVM/DBTO (60/40/1) blends: (a) ^1H NMR spectra; (b) DSC curves of Fraction III extracted from PA6/EVM/DBTO blends; and (c) ^1H NMR spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, the reaction temperatures for the ester–amide exchange reaction should be lower than 260°C ; otherwise, unexpected side reactions would occur very quickly.

It can be concluded that an ester–amide exchange reaction between PA6 and EVM can take place during melt compounding following the mechanism described in Scheme 3 and leading to the formation of a new graft copolymer, PA6-grafted EVM.

Composition and Structure of EVM-g-PA6 Copolymer

EVM-g-PA6 copolymer was separated from the PA6/EVM/DBTO (60/40/1, 60 min) blend (Scheme 1), and its grafting ratio and PA6 branch length were characterized. The PA6 content in EVM-g-PA6 was determined as 5.2 wt % by elemental analysis (Supporting Information Table S3). The molar grafting ratio (P_{mol}) is defined as the fraction of the acetate groups taking part in exchange reaction and calculated as 5.9 mol % based on the ^1H NMR results of PA6/EVM/DBTO (60/40/1, 60 min) blend [eq. (1)].

$$\text{VA exchange reaction ratio} = (2I_{2.40}/3I_{3.45})F_{\text{AB},0}/F_{\text{A1B1},0} \quad (1)$$

where $F_{\text{AB},0}$ and $F_{\text{A1B1},0}$ are the initial molar fractions of amide and acetate groups in the blends, respectively, and $I_{2.40}$ and $I_{3.45}$ are the relative intensities of signal peaks of methyl protons of acetamide groups formed by exchange reaction and methylene protons adjacent to amide amino groups of PA6, respectively.

In the NMR analysis of separated EVM-g-PA6, NMA was dissolved in $\text{CDCl}_3/\text{CF}_3\text{COOD}$ (1/1 v/v) solvent as an internal standard compound together with EVM-g-PA6. The mass of PA6 branches in EVM-g-PA6, m_p , was calculated as follows based on the characteristic proton ratio between PA6 and NMA.

$$m_p = \frac{m_{\text{NMA}}}{M_{\text{NMA}}} \left(\frac{3I_{3.45}}{2I_{3.04}} \right) M_A \quad (2)$$

where m_{NMA} and M_{NMA} are the mass and molar mass of NMA, respectively, M_A is the molar mass of structure unit of PA6, and $3I_{3.45}/(2I_{3.04})$ is the intensity ratio between the characteristic proton signal peaks of PA6 at 3.45 ppm and NMA at 3.04 ppm.

Supposed the mass of PA6 is m , the mass fraction of PA6 branches (P_{wt}) in EVM-g-PA6 was calculated using $P_{\text{wt}} = m_p/m$. P_{wt} is 2.1 wt % for PA6/EVM/DBTO (60/40/1, 60 min) blend and it is lower than that determined by elemental analysis. The molar grafting ratio P_{mol} (Figure 6) and the molar number of PA6 branches n_p are calculated as follows:

$$P_{\text{mol}} = \left(3 \frac{I_{4.97} - I_{2.18}}{I_{2.40} - I_{2.40}} \right) / \left(3 \frac{I_{4.97}}{I_{2.40}} + \frac{3}{2} \frac{I_{5.45}}{I_{2.40}} + 3 \frac{I_{5.16}}{I_{2.40}} \right) \quad (3)$$

$$= (3I_{4.97} - I_{2.18}) / \left(3I_{4.97} + \frac{3}{2}I_{5.45} + 3I_{5.16} \right)$$

$$n_p = \frac{m_{\text{NMA}}}{M_{\text{NMA}}} \left(3 \frac{I_{4.97}}{I_{2.40}} \right) \left(1 - \frac{I_{2.18}}{3I_{4.97}} \right) \quad (4)$$

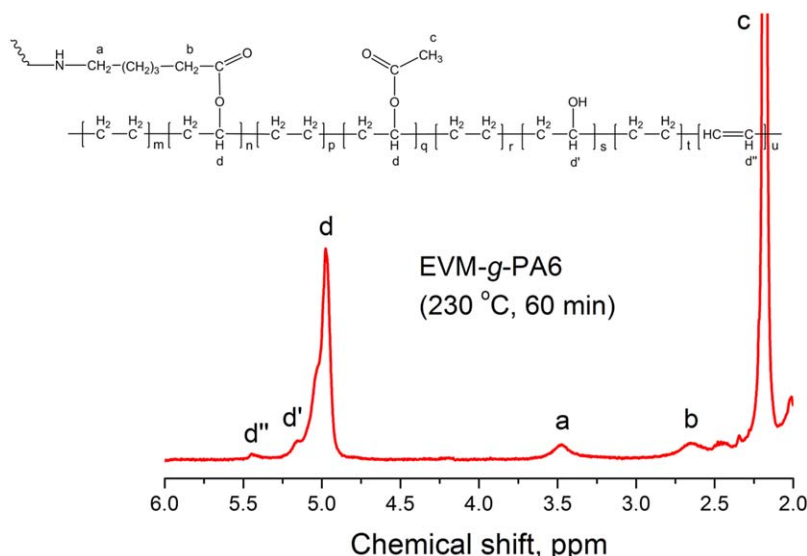
P_{mol} and n_p are 2.3 mol % and 5.40×10^{-7} mol for EVM-g-PA6 copolymer separated from PA6/EVM/DBTO (60/40/1, 60 min) blend, respectively.

$$\overline{M}_n = m_p/n_p = \frac{(3I_{3.45}/2I_{2.40})M_A}{(3I_{4.97}/I_{2.40})(1 - I_{2.18}/3I_{4.97})} = \frac{I_{3.45}M_A}{2(I_{4.97} - I_{2.18}/3)} \quad (5)$$

The number-average molecular weight of PA6 branches in EVM-g-PA6 is 278 g/mol as calculated from eq. (5), suggesting short grafted PA6 branches exist. Equation (5) provides a method based on ^1H NMR spectrum to calculate the branch

Table I. Effects of Reaction Conditions on the Exchange Reaction Extent

Blends	PA6/EVM (10 min)	PA6/EVM (20 min)	PA6/EVM/DBTO (10 min)	PA6/EVM/DBTO (20 min)	PA6/EVM/DBTO (40 min)	PA6/EVM/DBTO (60 min)
$\frac{2}{2.40}$ $\frac{3}{3.45}$	0.004	0.005	0.009	0.013	0.018	0.021

**Figure 6.** Section of the ^1H NMR spectra and chemical structure of EVM-g-PA6 copolymer extracted from PA6/EVM/DBTO (60/40/1, 60 min) blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

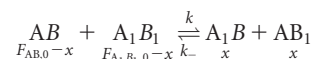
structure of graft copolymer, although the calculated results for EVM-g-PA6 copolymer have large deviation from those determined by elemental analysis owing to the relatively low PA6 content in the copolymer.

The composition and structure of EVM-g-PA6 copolymer prepared from the melt compounding of PA6/EVM are successfully characterized. The PA6 branch fraction and molecular weight of EVM-g-PA6 copolymer are about 5.2 wt % and 278 g/mol, respectively, for PA6/EVM (60/40) blend processed at 230°C for 60 min.

Exchange Reaction Kinetics

To understand the ester–amide reaction occurred between the backbone and side groups in PA6/EVM blends, the reaction kinetics were investigated in detail by considering the effects of catalyst, composition, and shearing action.

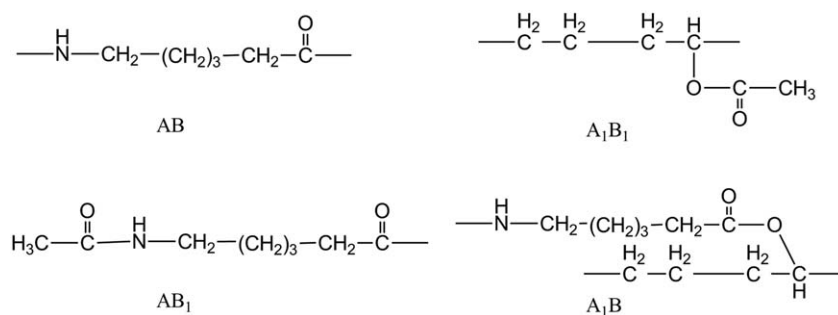
The Reaction Kinetic Equation. To investigate the reaction kinetics and parameters, a second-order reversible reaction is assumed as follows^{45–47}:



where the structures of AB, A_1B_1 , A_1B , and AB_1 are shown in Scheme 5, k and k_- stand for the forward and reverse reaction rate constants, $F_{AB,0}$ and $F_{A_1B_1,0}$ are the initial molar fractions of AB and A_1B_1 , respectively, and x is the molar fraction of reacted acetate group. Then, eq. (6) is obtained:

$$\frac{dx}{dt} = k(F_{AB,0} - x)(F_{A_1B_1,0} - x) - k_-x^2 \quad (6)$$

As this ester–amide exchange reaction is reversible and the chemical equilibrium constant of exchange reaction is close to

**Scheme 5.** The diad structure of reactants and reaction products.

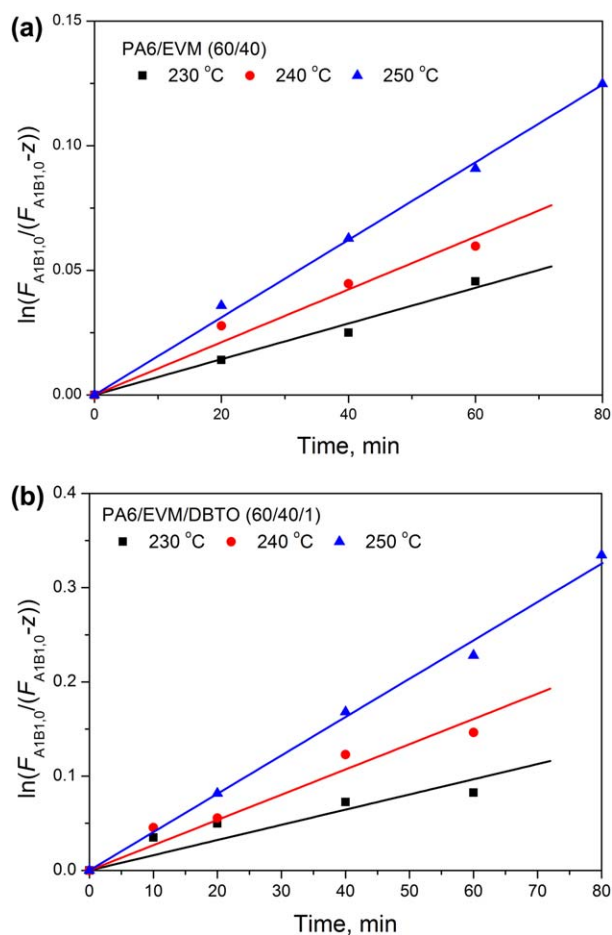


Figure 7. Plots of the kinetic expression of the ester–amide exchange reaction at different temperatures for (a) PA6/EVM (60/40) and (b) PA6/EVM/DBTO (60/40/1) blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

unity,^{48–50} eq. (6) could be transformed into the following expression as described in the Supporting Information:

$$\ln\left(\frac{F_{A_1B_1,0}}{F_{A_1B_1,0}-z}\right) = Kt \quad (7)$$

where $z = x/F_{AB}$, 0 and K is the exchange reaction rate constant. Thus, eq. (7) can be taken as the kinetic expression of the exchange reaction and the rate constant K can be obtained from the slopes of the fitting line by plotting $\ln[F_{A_1B_1,0}/(F_{A_1B_1,0}-z)]$ versus time, as shown in Figure 7(b). The rate constants for PA6/EVM/DBTO (60/40/1) blend were calculated as 1.61×10^{-3} , 2.68×10^{-3} , and $4.07 \times 10^{-3} \text{ min}^{-1}$ at 230, 240, and 250 °C, respectively. Then the rate constants were fitted linearly again $1/T$ according to Arrhenius expression [eq. (8)] to obtain the activation energy E_a and the pre-exponential factor A .

$$\ln K = \ln A - \frac{E_a}{RT} \quad (8)$$

where R is the gas constant with the value of 8.314 J/mol K and T is the absolute temperature. The calculated activation energy was 102 kJ/mol and the pre-exponential factor was $5.66 \times 10^7 \text{ min}^{-1}$ in the presence of catalyst DBTO.

Effect of Catalyst on the Reaction Kinetics. The reaction rate constants at 230, 240, and 250 °C for PA6/EVM (60/40) blend were calculated as 7.16×10^{-4} , 1.06×10^{-3} , and $1.56 \times 10^{-3} \text{ min}^{-1}$, respectively, as shown in Figure 7(a). The pre-exponential factor and activation energy were calculated as $4.95 \times 10^5 \text{ min}^{-1}$ and 85.1 kJ/mol for the PA6/EVM (60/40) blend. The higher rate constants for the PA6/EVM/DBTO (60/40/1) blend than those of PA6/EVM (60/40) blend are obviously caused by the presence of the catalyst DBTO.

In PA6/EVM (60/40) blend, the main exchange reaction should happen between active amino end groups in PA6 and acetate groups in EVM (the outer–inner exchange reaction), as the role of the active end groups has been confirmed in other reactive blends.^{8,10,19,51–53} In the presence of catalyst DBTO, the outer–inner exchange reaction and the inner–inner exchange reaction (direct exchange reactions between inner functional groups located inside of the polymer chains) both proceeded. Therefore, the activation energy of end group-activated exchange reaction was lower than that of DBTO-activated exchange reaction, which was a sum of these two reactions.

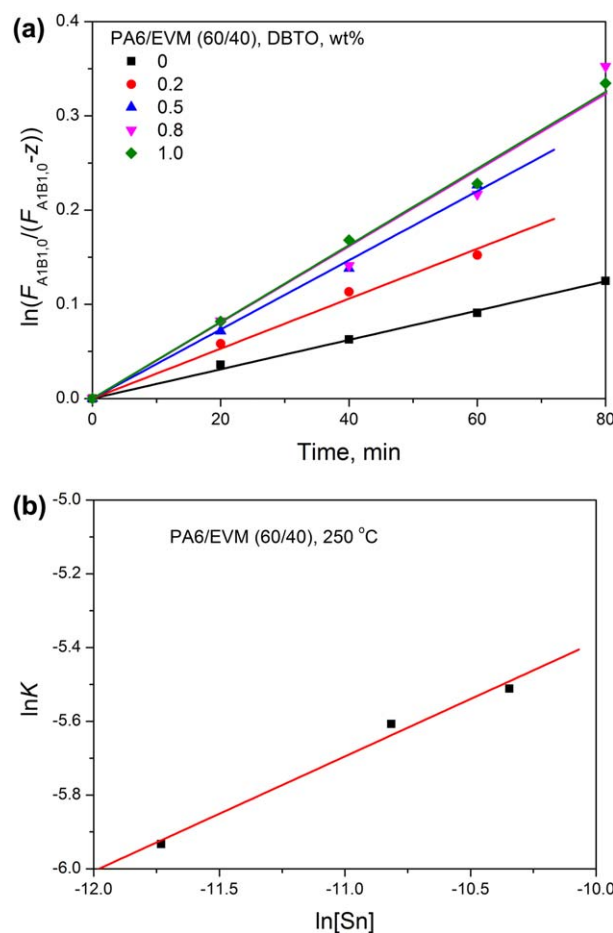


Figure 8. Plots of the kinetic expression, rate constant (a) and catalyst content index factor (b), of the ester–amide exchange reaction at different temperatures for the PA6/EVM blends with varied DBTO content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

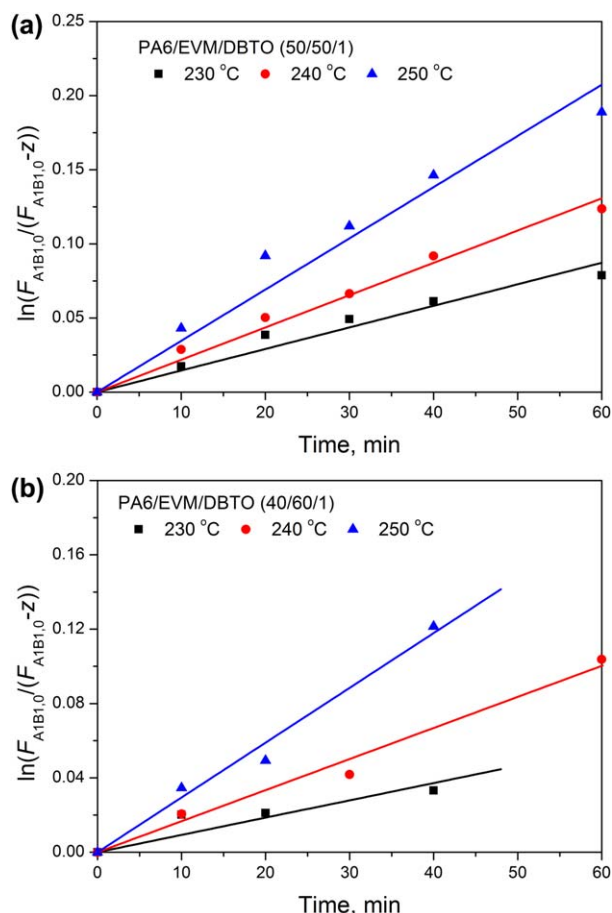


Figure 9. Plots of the kinetic expression of the ester–amide exchange reaction of PA6/EVM/DBTO blends with different PA6/EVM ratios: (a) 50/50 and (b) 40/60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For catalyzed exchange reactions, the reaction rate constant had a logarithmic relation to the catalyst concentration.^{47,50} To analyze the effect of DBTO content on the exchange reaction, the following modified kinetic equation was used:

$$K = A[\text{Sn}]^n e^{-E_a/RT} \quad (9)$$

$$\ln K = \ln A + n \ln [\text{Sn}] - \frac{E_a}{RT} \quad (10)$$

where [Sn] is the concentration of DBTO, mol per gram of polymer blend.

As shown in Figure 8, A was calculated by fitting $\ln K$ versus [Sn] [eq. (10)]. The dependence of rate constant K on DBTO

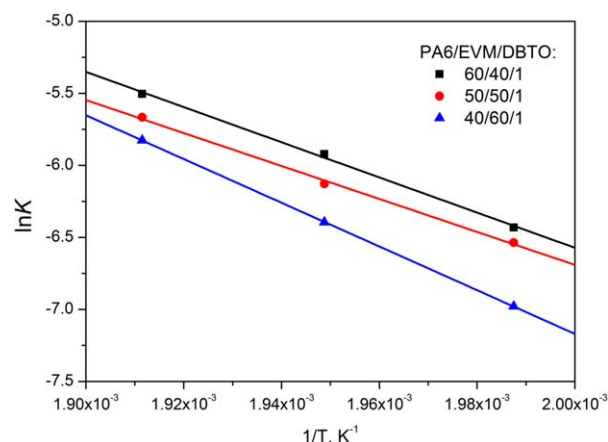


Figure 10. Plot of the Arrhenius expression for PA6/EVM/DBTO blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content and processing temperature for PA6/EVM blends can be described by the following relation:

$$K (\text{min}^{-1}) = 1.42 \times 10^9 [\text{Sn}]^{0.31} \exp(-1.02 \times 10^5 / RT) \quad (11)$$

Theoretically, K increased with increasing DBTO content at a specific temperature. In the experiment of this study, K increased slightly when the DBTO content was over 0.8 wt % (Figure 8). It should be due to the saturation of DBTO at the interface between PA6 and EVM, where the exchange reaction occurred, and some catalyst would diffuse from the interface into the inner part of the polymer melt.⁵⁴

Effect of PA6/EVM Ratio on the Kinetic Parameters. When the PA6/EVM ratio varied from 60/40 to 40/60, with the molar ratio of the reaction units approaching one, both the activation energy and pre-exponential factor increased (Figures 9 and 10, Table II). The ester–amide exchange reaction occurs at the interface between PA6 and EVM domains. As the PA6/EVM ratio approached to 40/60, the two phases were co-continuous [Supporting Information Figure S2(c)], where the interface area and the number of exchange collisions increased, thus caused the pre-exponential factor to increase.⁴⁵ The activation energy of PA6/EVM blends varied with increasing PA6/EVM ratio, presumably because PA6/EVM (40/60) blend has higher temperature dependency of melt viscosity than PA6/EVM (60/40, 50/50) blends.

Effect of Shearing Force on the Reaction Rate Constants. Exchange reactions of PA6/EVM/DBTO were carried out at both static and shearing conditions to investigate the effect of

Table II. The Component Ratio Dependence of Reaction Kinetic Parameters

PA6/EVM (weight ratio)		60/40	50/50	40/60
$K \times 10^3 (\text{min}^{-1})$	230°C	1.61	1.45	0.931
	240°C	2.68	2.18	1.67
	250°C	4.07	3.46	2.95
E_a (kJ/mol)		102	95.1	126
A (min^{-1})		5.66×10^7	1.07×10^7	1.17×10^{10}

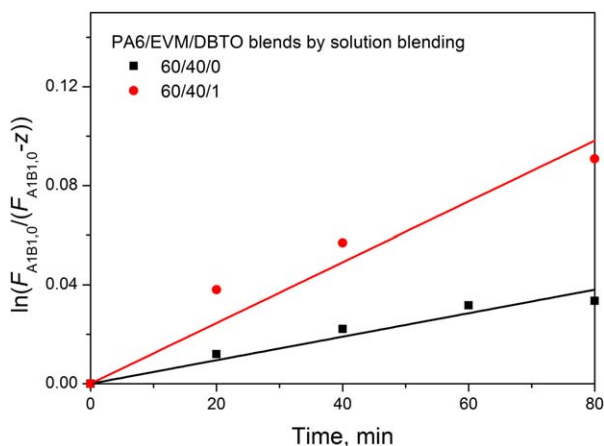


Figure 11. Plot of the reaction rate constants of the ester–amide exchange reaction at 250°C for PA6/EVM (60/40) and PA6/EVM/DBTO (60/40/1) blends prepared by solution blending. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shearing action on the reaction rate constant K . The PA6/EVM blends prepared by solution blending were heated isothermally at 250°C without shearing for different time, and K was 4.75×10^{-4} and $1.23 \times 10^{-3} \text{ min}^{-1}$ for PA6/EVM (60/40) and PA6/EVM/DBTO (60/40/1), respectively (Figure 11). But during melt compounding, K was 1.56×10^{-3} and $4.07 \times 10^{-3} \text{ min}^{-1}$ for PA6/EVM (60/40) and PA6/EVM/DBTO (60/40/1), respectively. Both K values of PA6/EVM and PA6/EVM/DBTO blends were increased owing to the shearing action during melt compounding. The shearing action enables to refresh the interface between PA6 and EVM, thus facilitating the exchange reaction at the interface.

Morphology and Mechanical Properties

The morphology development of the PA6/EVM/DBTO (60/40/1) blend is shown in Figure 12. The dispersed EVM phase gradually transformed to continuous phase when the mixing time increased from 10 to 20 min, until 60 min. This phenomenon may be caused by two reasons: the long-time shearing process at 230°C or the increased copolymer contents from 2.0 to 6.8% (Supporting Information Table S2). To further elucidate the phase transition behavior, the morphology development in PA6/EVM/DBTO (40/60/1) blends was investigated by SEM (Supporting Information Figure S3). It was found that the continuous EVM phase in the PA6/EVM (40/60) blend did not transform to dispersed phase when the reaction time increased from 10 to 60 min, which indicates that the effect of exchange reaction extent plays a major role in the morphology transition behavior in PA6/EVM/DBTO (60/40/1) blend.

The mechanical properties are listed in Table III. For the PA6/EVM/DBTO (60/40/1) blend, the tensile strength and elongation at break were increased by 19 and 22%, respectively, when the mixing time increased from 10 to 20 min, which should be related to the increased copolymer content and the co-continuous phase morphology. However, as the mixing time increased up to 60 min, the tensile strength decreased but elongation at break increased. This is consistent to the morphology changes shown in Figure 12 that the dispersed EVM phase

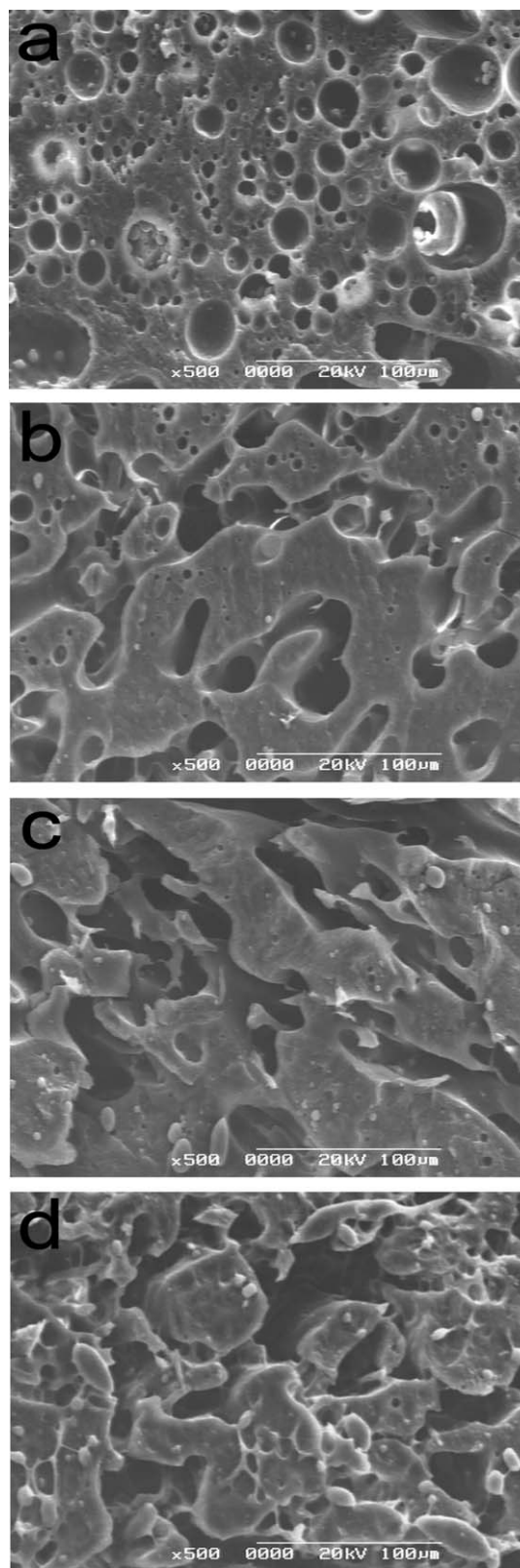


Figure 12. SEM images of cryogenically fractured surface of PA6/EVM/DBTO (60/40/1) blends (etched by acetone): (a) 10 min; (b) 20 min; (c) 40 min; and (d) 60 min.

Table III. Mechanical Properties of PA6/EVM/DBTO (60/40/1) Blends with Different Mixing Time

Reaction time (min)	Tensile strength (MPa)	Elongation at break (%)
10	16.3 ± 0.9	9 ± 2
20	19.4 ± 2.4	11 ± 3
40	8.3 ± 0.7	14 ± 4
60	7.1 ± 0.7	10 ± 4

transformed into a continuous phase. Therefore, to prepare high-performance PA6/EVM blends, higher reaction extent and shorter processing time are recommended to reduce the deterioration of properties of blends. The effects of processing conditions on the exchange reaction, for example, solution mixing or twin-screw extrusion, are under investigation in our group.

CONCLUSIONS

The ester–amide exchange reaction between PA6 and EVM during melt blending can take place at elevated temperatures, leading to the formation of the graft copolymer of PA6-grafted EVM and acetamide-terminated PA6. The PA6-grafted EVM was separated from PA6/EVM blends by solvent extractions, and its composition and structure were characterized by ¹H NMR, FTIR, and DSC analysis. Some side reactions of PA6/EVM blend during melt blending, i.e., the hydrolysis and elimination of acetate groups of EVM, were studied in detail, and their effect on the ester–amide exchange reaction kinetics was considered. The ester–amide exchange reaction was assumed as a second-order reversible reaction, and the dependence of rate constant and activation energy on catalyst DBTO content, PA6/EVM ratio, and shearing action was quantitatively investigated. An approximate rate constant relationship for the exchange reaction was derived for PA6/EVM (60/40) blend. Under the reaction condition of 230°C for 60 min, the reaction extent between PA6 and EVM, expressed by the percentage content of the acetate groups taking part in the exchange reaction, was 5.9 mol % and the yield of EVM-g-PA6 copolymer was 6.8 wt % for PA6/EVM/DBTO (60/40/1) blend. The number-average molecular weight of PA6 branches in EVM-g-PA6 was ~278 g/mol as evaluated from nuclear magnetic resonance spectra. The formation of EVM-g-PA6 copolymer at the interface induced the dispersed EVM phase to transform into continuous phase for PA6/EVM (60/40) blend in the presence of DBTO, and the tensile strength was increased when the reaction time was less than 20 min. The characterized mechanism of the ester–amide exchange reaction between PA6 and EVM in this article is fundamental in guiding the synthesis of new graft copolymers and the manufacturing of high-performance PA6/EVM thermoplastic elastomers for engineering applications.

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